PATENT SPECIFICATION 1,070,396

DRAWINGS ATTACHED.

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1,070,396

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COMPLETE SPECIFICATION.

Method of Depositing Metal Coatings in Holes, Tubes, Cracks, Fissures and the Like.

We, UNION CARBIDE CORPORATION, LINDE DIVISION, a New York corporation, of 270 Park Avenue, New York 17, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to gas plating of metals, and provides a method of depositing metal coatings uniformly on substrate surfaces having holes, tubes, cracks, fissures, cavities and similar inaccessible recessed areas therein by means of thermal decomposition of vaporized compounds of metals under conditions of repetitive variation of pressure.

It has long been difficult and frequently impossible to secure electrodeposition of metals evenly in holes, tubes, fissures, cavities and the like inaccessible places. It is equally difficult to accomplish this by other metal coating methods, for example by flame or arc spraying, or by vacuum metallizing. Plating by chemical immersion or reduction has been employed for depositing metal on the inside of tubular shapes but this method is limited as to the metals that can be deposited. Moreover, the speed of plating is slow, and the character of deposit is poor.

An example of the inadequacy of present coating techniques is the inability to produce satisfactory metal deposits in dead-end holes or fissures. Electroplating methods can accomplish this only by placing an electrode in such cavities, and this is impossible when the openings are small, and this method is otherwise impractical and uneconomical. Chemical immersion or reduction processes have also been employed for plating holes or cavities, but such methods as are currently used require circulation of the plating solution through the holes or fissures which is difficult to accomplish particularly where the hole or cavity is very small. Further, employing chemical reduction methods for plating metal it has been found that generally the metal deposit is exceedingly brittle. Similarly, it has been observed by test runs that vacuum deposition using spray coatings of metal are inapt because of the non-uniformity of the metal deposit produced and the impracticability of the method for depositing metal in small holes and crevices.

According to the invention there is provided a method of depositing metal on substrate surfaces having holes, crevices, small voids, cavities or dead end fissures therein, or bores extending therethrough, which method comprises the steps of introducing a thermally decomposable metal plating gas onto said surfaces to be plated with metal, heating said surfaces and contacting said surfaces with the plating gas while said surfaces are at a temperature to cause the decomposition of said plating gas and deposition of metal thereon, and subjecting said plating gas to pulsating pressure conditions in which said gas pressure is alternately and repetitively reduced and increased so that during a reduction in pressure gaseous decomposition products formed during the plating operation are withdrawn from the holes, crevices or the like to permit the re-entry therein of fresh thermally decomposable gases during a subsequent increase in gas pressure, whereby a uniform plating is simultaneously obtained on said surfaces and the holes, crevices or the like therein.

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Employing pulsating metal plating vapors during gas plating, in accordance with the invention, the metal is deposited throughout the walls of the bore, hole or cavity. Using non-pulsating gas plating methods, as in conventional gas plating practices, these improved plating results are not obtained. The process of the invention thus makes it possible to deposit metal coatings in such inaccessible areas by employing the modified gas plating process as described.

The pulsated gas pressure undulations or compression waves in the gas plating chamber may be produced in any suitable manner. For example, by alternately and repetitively creating a vacuum or rarified atmosphere in the plating chamber and then filling the chamber with vapors of the thermally decomposable metal bearing compound with or without the presence of a carrier gas or other vapors or gases.

Pulsation of the plating gas also may be accomplished by periodically shutting off and on the flow of the plating gas to the plating chamber or plating area. This method permits the gas pressure to build up behind the shut off point or valve, then upon opening of the valve the plating gas surges into the plating chamber or area to be plated, creating the pulsation. Use of moving walls or diaphragms, as well as sound waves may be employed, as desired, to produce the plating gas pressure pulsations while in contact with the area to be plated.

In the accompanying drawings:—

Figure 1 is a view in elevation, and partly in section, illustrating a suitable arrangement for carrying out a pulsating gas plating of an elongated article having a small central bore extending therethrough;

Figure 2 is a view in section of a modification for gas plating metal into dead end cracks and crevices;

Figure 3 illustrates in elevation a rotary valve useful for periodically interrupting the flow of plating gas to the plating chamber;

Figure 4 illustrates a modification of the arrangement shown in Figure 1, and where two solenoid operated valves are utilized; and

Figure 5 illustrates a still further modification where the pulsation of gases in the plating chamber is subjected to sonic wave vibrations during gas plating.

Referring to the drawings in more detail, in Figure 1 the gas plating arrangement shown comprises a metal rod 10 having a small diameter bore 11 which extends the length of the rod from an inlet opening 14 to an outlet opening 15.

Connected at the inlet 14 is a conduit 17 having an adapter portion 18 hermetically sealed thereto, the conduit being connected to a pressurized source of nickel carbonyl vapors. A solenoid operated valve 20 in the conduit 17 controls the passage of gaseous carbonyl passing to the bore 11 from the source through pipe 21 and conduit 17. An exhaust line 23 is connected to the outlet opening 15. Waste gases are preferably passed to a condenser, not shown, and the re-usable portions recirculated back to the metal carbonyl source or generator for return to the gas plating system.

An electrical heating coil 25 is utilized to heat the rod 10 to a temperature high enough so that the walls of the bore 11 are about 400°F so that the gaseous nickel carbonyl is thermally decomposed in the bore.

To cause pressure pulsation of the plating carbonyl gas, the solenoid valve 20 is repeatedly opened and closed by a motor driven electrical timer 27. Quick opening and closing of the valve sets up pulsations of the plating carbonyl gas in the bore so that substantially uniform deposition of metal occurs throughout the length of the bore.

In place of a solenoid operated valve, a rotary valve 29, such as illustrated in Figure 3, may be used.

In the pulsated gas plating arrangement shown in Figure 2, a modified rectangular plating chamber 32 is illustrated having side walls 34 and 35 hermetically sealed, as at 36 and 37, to a casting 40 whereby a crack or crevice 42 is enclosed. Metal plating gas flows from a pressurized source through the pulsating valve 44, inlet conduit 45 and into the plating chamber 46 and is pulsated into the crevice 42 where the metal bearing gas is decomposed to deposit the metal in the crevice. Waste gas is discharged from the plating chamber through conduit 48.

Referring to the pulsating gas plating arrangement illustrated in Figure 4 is a modification of that shown in Figure 1. In the modification a gas plating chamber 50 is provided with an inlet 52 and an outlet 54 through which pulsating gas plating vapors are conducted to the plating chamber and the waste gases from the chamber. The inlet 52 is connected to a solenoid operated valve 56 which in turn is connected with a heated expansion compartment 57 for vaporizing the metal carbonyl admitted thereto from a pressurized source as indicated by the arrow in Figure 4. For heating the compartment 57 a heater coil 58 is provided, the heating being kept below the temperature which would cause the metal bearing gas to decompose. In the use of metal carbonyls the temperature of this compartment is just enough to vaporize the metal carbonyl.

A second solenoid operated valve 60 is connected to the outlet 54 of the plating chamber for controlling the flow of waste gas from the plating chamber. Both valves

are suitably operated electrically by a motorized rotatable electrical timing switch mechanism 62. The exhaust line 63 is connected to a vacuum pump. A pattern 65 shaped of plater of paris and having graphite coated contour surfaces 66 for reproduction, is disposed in the plating chamber 50. To heat the pattern a resistance heater element 67 is suitably arranged in the bottom of the plating chamber and heat insulated therefrom to prevent metal from being deposited thereon. Deposited metal from decomposition of the gaseous metal compound, as illustrated at 70, forms a metal reproduction of the pattern or mold surface 66.

To provide a pulsating plating gas mixture in the plating chamber during the process, the vacuum pump and timing switch means 62 are operated to evacuate the plating chamber and intermittently open and close the valves 56 and 60 as described in Example 2. Using nickel carbonyl as the plating gas, a substantially uniform deposit of metal on the substrate pattern surface is achieved.

In Figure 5 a modified plating arrangement is shown wherein use is made of a sonic vibrator for creating a pulsating gas plating atmosphere. In this arrangement the plating chamber 75 is provided with an inlet 77 and an outlet 78, for introducing metal plating gas, as indicated by the arrows on the drawings. Preferably the plating chamber is dome-shaped and equipped with a sonic vibrator 80 which is electrically actuated by a motor 81. During gas plating the sonic vibrator is actuated to create sound waves of relatively low frequency, e.g., 10 to 40 cycles per second (c.p.s.) and preferably 10 to 20 c.p.s. is employed.

A mold or pattern shape 84 is arranged in the plating chamber 75 and is suitably heated as by a resistance heater 86 disposed beneath the pattern. The sonic pulsations created during the gas plating improves the metal deposited, as at 88, whereby greater depth of metal deposition is effected in the contours and indentations of the substrate pattern surface than is obtained without the use of sonic pulsations. Utilizing such a sonic pulsated plating gas improved deposits of metal on the pattern are obtained, particularly in recesses and corners which are ordinarily difficult to metal plate satisfactorily. It may be desirable to use a sonic vibrator in conjunction with the arrangements described with reference to Figures 1 to 4.

The pressure variations to produce pulsation of the plating gas are preferably accomplished with some degree of speed; otherwise with a steady moderate flow of vapors and gases suitable for thermally depositing coatings, the coating will tend to build up heavily on the first heated surface contacted, and depleting from the plating gas mixture the vapors of the metal compound, whereby succeeding areas contacted by the resultant metal-depleted gas, plate at a much slower rate.

The following examples are exemplary of how the process of the invention may be utilized.

EXAMPLE 1.

Nickel metal is deposited on the walls of a "through" bore of 1/16 inch in diameter in a brass forging approximately two inches in length. This is accomplished by heating the forging externally to approximately 400°F, and passing mixture of carbon monoxide and vaporized nickel carbonyl through the bore. A solenoid operated valve, as illustrated in Figure 1, is used to control passage of the plating gas mixture to the bore, the motorized electrical timing switch is set to cause the valve to remain open one second and then closed for one second. This operation is repeated to bring about pulsation of the plating gases. The process is continued for about 20 minutes or until about 0.005", of nickel is deposited in the bore, with a thickness variation of 0.001".

During operation of the process, when the solenoid operated valve is closed, pressure of the plating gas accumulates behind it and upon opening of the valve, a quick puff of the plating gas mixture flows through. If the valve is left open and the plating is continuous, the metal deposit tends to build up at the bore or hole entrance and drops off substantially at the exit.

EXAMPLE 2.

In this instance a casting having crack or dead-end fissure in the same is subjected to a pulsating gas as illustrated in Figure 2, and employing a vacuum pump connected to the exhaust. The plating is carried out similarly as described in Example 1, with a solenoid operated valve connected at the inlet to the plating chamber, the latter enclosing the surface portion of the casting. The pulsating plating gas penetrates into the crack and metal is deposited upon heating the casting while the pulsating metal bearing gas is brought in contact with the cracked casting area.

EXAMPLE 3.

In this example, a pulsating gas plating apparatus, such as illustrated in Figure 4, is employed to gas plate nickel on a mold pattern to form a replica thereof. The pattern, which is formed of a low melting alloy comprises a spherical-shaped article having small fissures extending over the surface, some of which extend to a depth of 3/8 of an inch. By heating the mold surface in a vacuum pump equipped chamber

to 400°F and exposing the heated mold surface to pulsating nickel carbonyl vapors, nickel metal is deposited in the fissures. Without pulsating the plating gas and simply heating and contacting the pattern with the plating gas scarcely any nickel metal is deposited in the fissures.

The inlet to the plating chamber is provided with a solenoid operated valve which is actuated periodically to admit vapors of nickel carbonyl in a pulsating manner. The outlet to the plating chamber is suitably connected through a second solenoid actuated valve to a vacuum pump. Both of the valves are operated electrically by a motorized rotating electrical timing switch. A heated expansion compartment is connected into the line between the nickel carbonyl source and the plating chamber to assure that the nickel carbonyl will be completely vaporized before entering the gas plating chamber, the metal carbonyl being heated in the expansion compartment to a temperature below that at which the same decomposes.

In carrying out the pulsated gas plating using the apparatus described, after the space in the lines and the gas plating chamber is filled with carbon dioxide, the vacuum pump and timing switch are turned on. With the inlet solenoid valve closed and the outlet valve open, the plating chamber is exhausted in 30 seconds to provide a vacuum pressure of 28 inches of Hg. Meanwhile the heated expansion chamber fills with vapors of nickel carbonyl. At the end of the 30 second interval, the timing switch opens the inlet valve and closes the exhaust valve, permitting vapors to rush in and fill the chamber. After a brief interval of 10 or 20 seconds, the inlet valve is closed, the exhaust valve opened, and the cycle repeated continuously.

Nickel is deposited to a thickness of 1/16 inch to 1/8 inch on the pattern substrate surface, and nickel is found to have deposited in the fissures, tapering off, at their bottoms to about half the thickness of the exposed flat area. In contrast to this, it was observed that when no pulsation of the plating gas was employed, the metal deposited in the fissures tapered off to nothing at the bottom.

EXAMPLE 4.

In this example a copper tubing approximately 10 feet in length and having O.D. of 3/8 inch and I.D. of 1/4 inch is gas plated in the interior wall surface with aluminum. This is accomplished by washing the tube in grease solvent such as naphtha and then heating the tube to about 800°F and while thus heated passing hydrogen gas therethrough to reduce surface oxides. The temperature of the tubing is then lowered to 500° to 600°F and the cleaned and degreased tube is subjected to a pulsating plating gas comprising vapors of aluminum triisobutyl. For the purpose of admitting the hydrogen, a three-way valve may be used which is operated initially to admit hydrogen gas, then the valve is turned to cut-off the hydrogen and admit the plating gas to the plating chamber.

The plating arrangement, as illustrated in Figure 1, is used to plate the interior of the copper tubing with aluminum. The solenoid operated valve is operated continuously by a motorized timing switch as heretofore described, whereby the valve is open for 2 seconds and closed for 5 seconds. The volume of plating gases is so adjusted that the pressure build-up during the 5 second interval when the valve is closed is enough to generate a puff of gases that more than fills and flushes the tube when the valve is opened. The composition of the plating gas found useful comprised, by volume, 50% argon, 30% isobutylene gas, 19.75% triisobutyl aluminum vapor and 0.25% oxygen.

After carrying out gas plating under these pulsating conditions, for 10 minutes, a deposit of aluminum in the tube of 0.001" thickness was obtained, the thickness of the deposit varied but about 20% from inlet to outlet.

EXAMPLE 5.

A ceramic block is gas plated with iron using a pulsating plating gas of iron carbonyl vapor. The ceramic body is first heated to a temperature of between 400°—500°F while enclosed in a pressure chamber freed of air and filled with the plating gas, the latter comprising a mixture approximating hydrogen 10%, carbon dioxide 65%, and containing approximately 25% iron carbonyl vapor by volume.

The iron carbonyl plating gas is rapidly injected into the gas plating chamber in one or two seconds to build up pressure to 200 pounds per square inch (p.s.i.). At this pressure and temperatures, the plating rate of iron is slow enough to permit plating gas mixture to permeate the pores of the ceramic body before deposition of the metal takes place. After the pressure has been built up as described, it is lowered rapidly and the ceramic block allowed to remain at atmospheric pressure for 10 seconds. Deposition of iron then occurs in the interior of the ceramic block and in the pores. Thereafter the pressure is again rapidly built up to 200 p.s.i. and the cycle repeated until iron becomes deposited throughout the ceramic body.

EXAMPLE 6.

In this instance a mass of copper balls approximately one-half inch in diameter is

subjected to gas plating as described in Example 1. Employing the pulsating gas plating method of this invention, nickel metal is deposited between the copper balls to bond the same together. When the gas plating was carried out without pulsation of the plating gas, substantially all the metal was deposited at or near the point where the plating gas entered the mass of balls and was not relatively evenly distributed between the balls as when employing the pulsating plating gas.

EXAMPLE 7.

In this instance a heavy nickel deposit is gas plated on an irregular-shaped plaster pattern. The pattern is heated to 300°—400°F. and contained in an airtight gas plating chamber. Plating gases consisting of nickel carbonyl vapors admixed with helium carrier gas are passed through the gas plating chamber after purging it free of air. Pulsations of the gas plating gas is produced by employing a vibratable diaphragm or suitable member, such as illustrated in Figure 5, and which generates sonic waves. These waves consist of alternate rarefactions and condensations. The pulsating waves in the plating gas chamber move the plating gas about the irregular contours of the pattern without which stratification and non-uniform plating tends to occur.

By the above means substantially improved coverage of the pattern is obtained, particularly in recesses and corners.

The invention, as heretofore pointed out, is concerned with gas plating metals employing thermally decomposable metal bearing compounds. In the specification and claims it will be understood that a thermally decomposable metal plating gas refers to a gaseous compound of a metal which decomposes when heated to a predetermined temperature range. The term plating gas connotes a gaseous mixture containing a thermally decomposable metal bearing compound, and such as may be admixed with other gases, such as a reducing gas, e.g., hydrogen, carbon monoxide, and/or a non-reactive carrier gas, for example carbon dioxide, nitrogen, methane, helium, argon and the like.

WHAT WE CLAIM IS:—

1. A method of depositing metal on substrate surfaces having holes, crevices, small voids, cavities or dead end fissures therein, or bores extending therethrough, which method comprises the steps of introducing a thermally decomposable metal plating gas onto said surfaces to be plated with metal, heating said surfaces and contacting said surfaces with the plating gas while said surfaces are at a temperature to cause the decomposition of said plating gas and deposition of metal thereon, and subjecting said plating gas to pulsating pressure conditions in which said gas pressure is alternately and repetitively reduced and increased so that during a reduction in pressure gaseous decomposition products formed during the plating operation are withdrawn from the holes, crevices or the like to permit the re-entry therein of fresh thermally decomposable gases during a subsequent increase in gas pressure, whereby a uniform plating is simultaneously obtained on said surfaces and the holes, crevices or the like therein.

2. A method as claimed in Claim 1, wherein said pulsating pressure of the plating gas is effected by alternately and repetitively creating a vacuum in the atmosphere of the surfaces to be plated with metal.

3. A method as claimed in Claim 1, wherein said pulsating pressure of the plating gas is effected by periodically shutting off and on the flow of the plating gas to the surfaces being treated.

4. A method as claimed in Claim 1, wherein said pulsating pressure is created by sonic waves set up in said plating gas.

5. A method as claimed in any preceding claim, in which said pulsating gas contains vaporized nickel metal carbonyls.

6. A method as claimed in any preceding claim, wherein said pulsating gas consists of a mixture of metal carbonyl and non-reactive carrier gas.

7. A method as claimed in any preceding claim, wherein said pulsating plating gas consists of a mixture of nickel carbonyl and carbon dioxide.

8. A method as claimed in any preceding claim in which the surfaces to be plated are heated to a temperature of approximately 400°F.

9. A method of depositing metal on substrate surfaces having holes, crevices, small voids, cavities or dead end fissures therein, or bores extending therethrough, which method is substantially as described with reference to the accompanying drawings.

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Fig.1

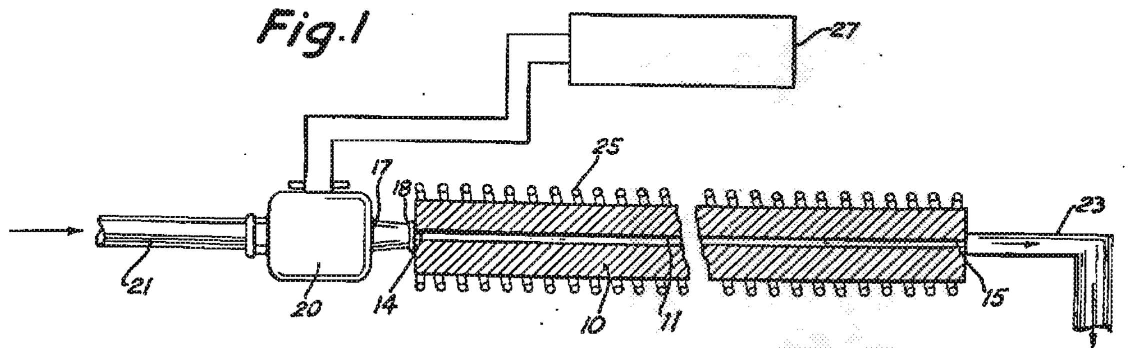


Fig.2

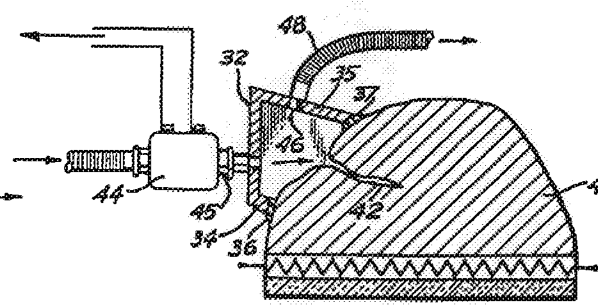
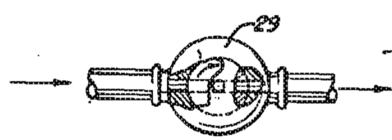


Fig.3



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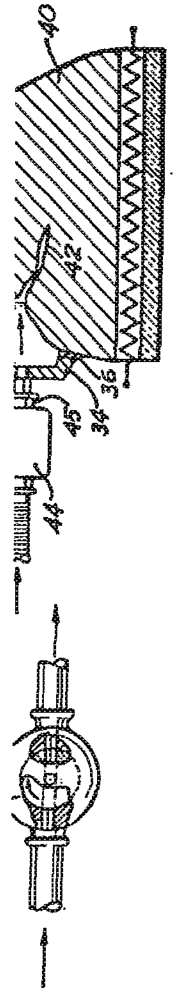
Sheets 1 & 2



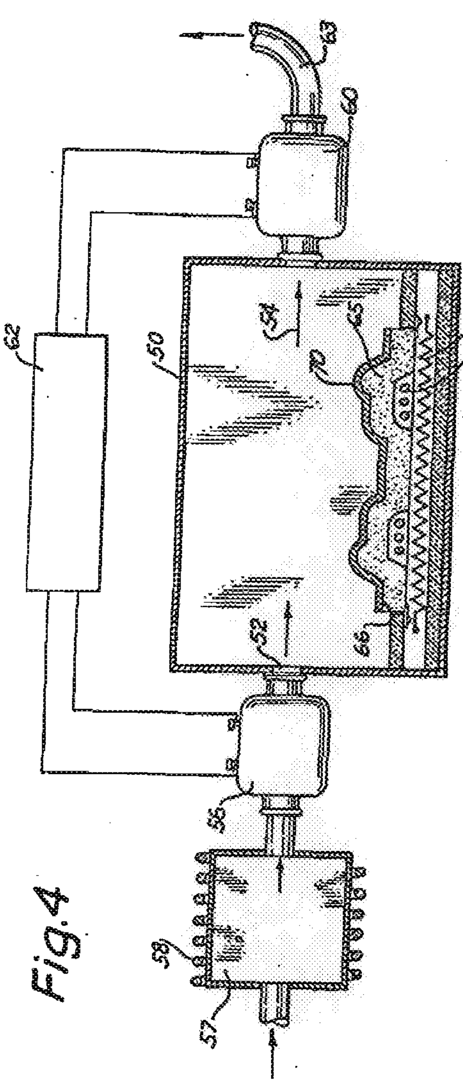


Fig.4

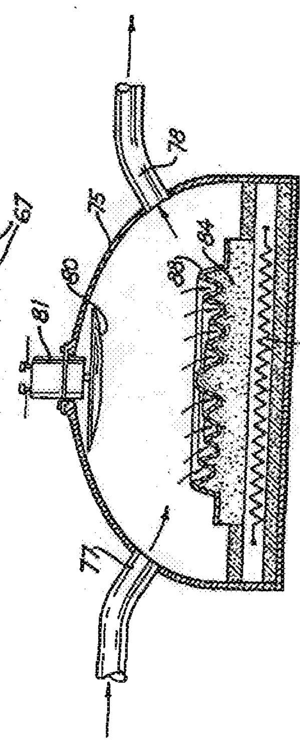


Fig.5

1070396 COMPLETE SPECIFICATION

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